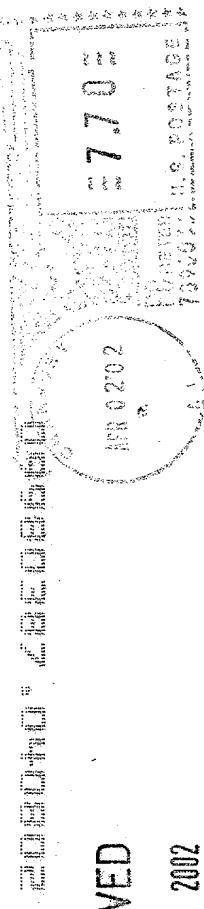


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Form PTO-1390 REV.10-94)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEYS DOCKET NUMBER RN99060
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/elected office (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		U.S. APPLICATION NO. <small>(IF KNOWN, SEE 37 CFR 1.5)</small> 09/980387 NOT APPLICABLE		
INTERNATIONAL APPLICATION NO. PCT/FR00/01438	INTERNATIONAL FILING DATE May 26, 2000	PRIORITY DATE CLAIMED June 04, 1999		
TITLE OF INVENTION PROCESS FOR SYNTHESIZING POLYMERS BY CONTROLLED FREE-RADICAL POLYMERIZATION WITH THE AID OF HALOGENATED XANTHATES				
APPLICANT (S) FOR DO/EO/US: Mathias DESTARAC, Dominique CHARMOT, Samir ZARD and Xavier FRANCK				
Applicant herewith submits the United States Designated/Elected Office (DO/EO/US) the following items and other information:				
1 <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371 2 <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371 3 <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371) (f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371 (b) and PCT Articles 22 and 39(1) 4 <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date 5 <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US) 6 <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). 7 <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210) 8 <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(2)). a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made, however the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 9 <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 10 <input checked="" type="checkbox"/> A oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). (unsigned) 11 <input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409). 12 <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 				
Items 13 to 18 below concern document(s) or information included: 13 <input type="checkbox"/> An information Disclosure Statement under 37 CFR 1.97 and 1.98 14 <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included 15 <input checked="" type="checkbox"/> A FIRST preliminary amendment 16 <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment 17 <input type="checkbox"/> A substitute specification. 18 <input type="checkbox"/> A change of power of attorney and/or address letter 19 <input checked="" type="checkbox"/> Certificate of Mailing by Express Mail 20 <input checked="" type="checkbox"/> Other items or information				
Forms PCT/IB/308 and 332, PCT/ISA/ 210 (English & French Version), PCT/IPEA/ 409, PCT/FR00/01438 as published				

US APPLICATION NO. <small>IF KNOWN, SEE 37 CFR 1.10</small> 09/900387		International Application No. PCT/FR00/01438	ATTORNEY DOCKET NUMBER RN99060										
CALCULATIONS PTO ONLY													
<p>21 The following fees are submitted:</p> <p>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</p> <table> <tr> <td><input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1,482) nor International search fee (37 CFR 1.445(a)(2) paid to USPTO and International Search Report not prepared by the EPO or JPO.....</td> <td>\$ 1,040.00</td> </tr> <tr> <td><input checked="" type="checkbox"/> International preliminary examination fee not paid to USPTO but International Search Report prepared by the EPO or JPO.....</td> <td>\$ 890.00</td> </tr> <tr> <td><input type="checkbox"/> International preliminary examination fee (37 CFR 1,482) not paid to USPTO but international search (37 CFR 1,4445 (a)(2)) fee paid to USPTO.....</td> <td>\$ 740.00</td> </tr> <tr> <td><input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1,482) but all claims did not satisfy provisions of PCT Article 33(1)-(4)</td> <td>\$ 710.00</td> </tr> <tr> <td><input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1,482) and all claims satisfied provisions of PCT Article 33(2)-(4)</td> <td>\$ 100.00</td> </tr> </table> <p>ENTER APPROPRIATE BASIC FEE AMOUNT =</p>				<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1,482) nor International search fee (37 CFR 1.445(a)(2) paid to USPTO and International Search Report not prepared by the EPO or JPO.....	\$ 1,040.00	<input checked="" type="checkbox"/> International preliminary examination fee not paid to USPTO but International Search Report prepared by the EPO or JPO.....	\$ 890.00	<input type="checkbox"/> International preliminary examination fee (37 CFR 1,482) not paid to USPTO but international search (37 CFR 1,4445 (a)(2)) fee paid to USPTO.....	\$ 740.00	<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1,482) but all claims did not satisfy provisions of PCT Article 33(1)-(4)	\$ 710.00	<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1,482) and all claims satisfied provisions of PCT Article 33(2)-(4)	\$ 100.00
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<p>Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1,492(e)).</p> <table> <tr> <td>\$ 890.00</td> <td></td> </tr> <tr> <td>\$ 0.00</td> <td></td> </tr> </table>				\$ 890.00		\$ 0.00							
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CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE										
Total Claims	19-20=	0	X\$18.00										
Independent Claims	3-3=	0	X\$84.00										
MULTIPLE DEPENDENT CLAIMS(S) (if applicable)		N/A	<input type="checkbox"/>										
			TOTAL OF ABOVE CALCULATIONS =										
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28)			<input type="checkbox"/>										
			SUBTOTAL =										
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1,492 (f)).			<input type="checkbox"/>										
			TOTAL NATIONAL FEE =										
Fee for recording the enclosed assignment (37 CFR1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property + <input type="checkbox"/>			<input type="checkbox"/>										
			TOTAL FEES ENCLOSED =										
			Amount to be refunded										
			charged										
<p>a <input type="checkbox"/> A check in the amount of \$ _____ to cover the above fees is enclosed</p> <p>b <input checked="" type="checkbox"/> Please charge my Deposit Account No. 18-1171 in the amount of \$890.00 to cover the above fees.</p> <p>c <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 18-1171 A duplicate copy of this sheet is enclosed.</p>													
<p>NOTE: Where an appropriate time limit under 37 CFR 1,494 or 1,495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.</p>													
<p><u>John Daniel WOOD</u> SIGNATURE</p>													
<p>SEND ALL CORRESPONDENCE TO: John Daniel WOOD</p>													
<p>RHODIA INC. 259 Prospect Plains Road CN 7500 Cranbury, NJ 08512</p>													
<p><u>November 30, 2001</u></p>		<p>John Daniel WOOD NAME 31,146</p>											
<p>DATE</p>		<p>REGISTRATION NUMBER</p>											



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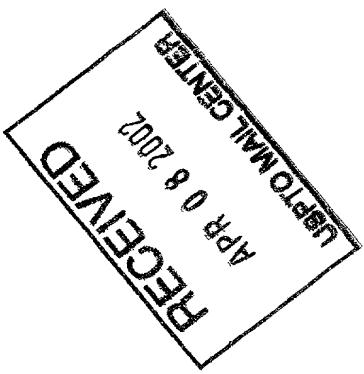
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Application Serial No. 09/980,387

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the Application of: Mathias DESTARAC, Dominique CHARMOT, Samir ZARD, and Xavier FRANCK

National Phase of PCT/FR00/01438

Examiner: N/A

International Filing Date : May 26, 2000

Serial No: To be assigned

Art Unit: N/A

Filing Date: To be assigned

For: PROCESS FOR SYTHESIZING POLYMERS BY CONTROLLED FREE-RADICAL POLYMERIZATION WITH THE AID OF HALOGENATED XANTHATES

Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Dear Sir:

Prior to calculation of filing fee, please enter the following amendment in the specification and claims:

In the Specification:

Page 1, just after the title, please add the new following paragraph:

This application is an application under 35 U.S.C. Section 371 of International Application Number PCT/FR00/01438 filed on May 26, 2000.

In the Claims:

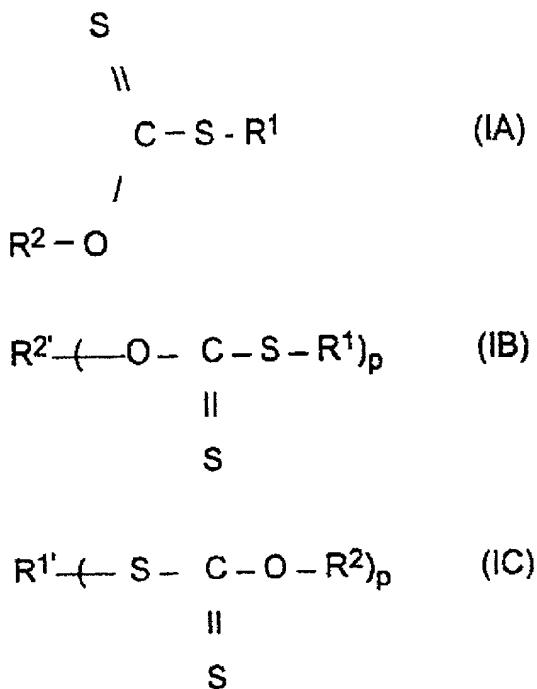
Please cancel claims 1-16, and replace them with the following new claims 17-35.

17. (New) A process for preparing polymers, comprising to steps of:

a) bringing into contact to obtain a polymer:

- at least one ethylenically unsaturated monomer,
- at least one source of free radicals, and

- at least one compound of general formula (IA), (IB), or (IC):



wherein:

- R^2 and R^2' represent:

- an alkyl, acyl, aryl, alkene, or alkyne group (i),
- a carbocyclic system (ii), saturated or unsaturated, optionally aromatic,

or

- a heterocyclic system (iii), saturated or unsaturated,

these groups and cyclic systems (i), (ii), and (iii) being substituted by at least one fluorine atom, chlorine atom, or bromine atom,

- R^1 and R^1' represent:

- an alkyl, acyl, aryl, alkene, or alkyne group (i), optionally substituted,

- a carbocyclic system (ii), saturated or unsaturated, optionally substituted or aromatic,
- a heterocyclic system (iii), saturated or unsaturated, optionally substituted,

these groups and cyclic systems (i), (ii) and (iii) being optionally substituted by substituted phenyl groups, substituted aromatic groups, alkoxy carbonyl or aryloxy carbonyl (-COOR) groups, carboxy (-COOH) groups, acyloxy (-O₂CR) groups, carbamoyl (-CONR₂) groups, cyano (-CN) groups, alkyl carbonyl groups, alkyl aryl carbonyl groups, aryl carbonyl groups, aryl alkyl carbonyl groups, phthalimido groups, maleimido groups, succinimido groups, amidino groups, guanidino groups, hydroxyl (-OH) groups, amino (-NR₂) groups, halogen atoms, allyl groups, epoxy groups, alkoxy (-OR) groups, S-alkyl groups, S-aryl groups, or groups having hydrophilic or ionic character, R representing an alkyl or aryl group, or

- a polymer chain,

- p is between 2 and 10, and

b) recovering the polymer.

18. (New) A process according to claim 17, wherein the group having hydrophilic or ionic character is selected from the group consisting of alkali metal salts of carboxylic acids, the alkali metal salts of a sulfonic acid, polyalkylene oxide chains, and quaternary ammonium salts.

19. (New) The process according to claim 17, wherein R² and R^{2'} are substituted by at least one fluorine atom.

20. (New) The process according to claim 17 wherein R² represents a group of formula: -CH₂R^{5'}, wherein R^{5'} represents an alkyl group substituted by at least one fluorine atom, chlorine atom, or bromine atom.

21. (New) The process according to claim 17, wherein R² is selected from the group consisting of the following groups:

- CH₂CF₃,
- CH₂CF₂CF₂CF₃ and
- CH₂CH₂C₆F₁₃.

22. (New) The process according to claim 17, wherein R¹ represents:

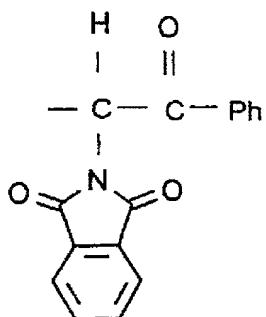
- a group of formula CR^{1'}R^{2'}R^{3'}, wherein:
 - R^{1'}, R^{2'} and R^{3'} represent the groups (i), (ii), or (iii), or
 - R^{1'} = R^{2'} = H and R^{3'} is an aryl, alkene, or alkyne group, or
- a group of formula -COR^{4'}, wherein R^{4'} represents a group (i), (ii), or (iii).

23. (New) The process according to claim 22, wherein R¹ is selected from group consisting of the following groups:

- CH(CH₃)(CO₂Et),
- CH(CH₃)(C₆H₅),
- CH(CO₂Et)₂,
- C(CH₃)(CO₂Et)(S-C₆H₅),

- $\text{C}(\text{CH}_3)_2(\text{C}_6\text{H}_5)$, and

-



24. (New) The process according to claim 17, wherein step a) comprises bringing into contact a compound of formula (IA).

25. (New) The process according to claim 24, wherein the compound of formula(IA) is selected from the group constisting of ethyl a-(O-heptafluorobutylxanthyl)propionate, ethyl a-(O-trifluoroethylxanthyl)propionate, and ethyl a-(O-tridecafluorooctanylxanthyl)propionate.

26. (New) The process according to claim 17, wherein the ethylenically unsaturated monomer is selected from the group consisting of styrene or its derivatives, butadiene, chloroprene, (meth)acrylic esters, and vinyl nitriles.

27. (New) The process as according to claim 26, wherein the ethylenically unsaturated monomer is selected from the group consisting of vinyl acetate, vinyl Versatac®, and vinyl propionate.

28. (New) A polymer obtained by the process which essentially consists in bringing an ethylenically unsaturated monomer into contact with a source of free radicals and a compound of formula (IA), (IB), or (IC) as defined in claim 17.

29 (New) The polymer according to claim 28, having a polydispersity index of at most 2.

30. (New) The polymer according to claim 29, wherein the polydispersity index is of at most 1.5.

31. (New) A process for preparing multiblock polymers, comprising the following steps:

- step 1: carrying out step a) according to claim 17, to obtain a block polymer
- step(s) 2: repeating at least once the preceding step with different monomers from the preceding step, and with the block polymer obtained from the preceding step instead of the precursor compound of formula (IA), (IB), or (IC), to obtain a multiblock polymer, and
- step 3: recovering the multiblock polymer.

32. (New) A multiblock polymer obtained by the process according to claim 31.

33. (New) The multiblock polymer according to claim 32, having an index of polydispersity of at most 2.

34. (New) The multiblock polymer according to claim 33, wherein the index of polydispersity is of at most 1.5.

35. (New) A multiblock polymer according to claim 32, comprising at least two polymer blocks selected from the group consisting of the following associations of blocks:

- polystyrene and polymethyl acrylate,
- polystyrene and polyethyl acrylate,

- polystyrene and polytert-butyl acrylate,
- polyethyl acrylate and polyvinyl acetate,
- polybutyl acrylate and polyvinyl acetate, and
- polytert-butyl acrylate and polyvinyl acetate.

REMARKS

The preliminary amendments are filed to comply with the claims structure and wording according to the United States Patent law. It is asserted that these amendments do not add new matter. Support for these amendments can be found in the specification and claims as originally filed.

New claims find basis as mentioned in the chart below:

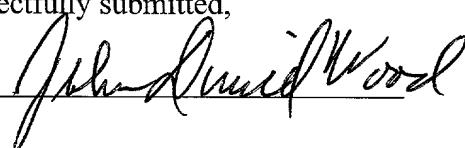
<u>New Claims</u>	Basis	
	In the claims as filed	In the specification
17	1	
18	1	
19	2	
20	3	
21	4	
22	5	
23	6	
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27	10	
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32	14	
33	15	
34	15	
35	16	

RN99060
Preliminary Amendment
PCT/FR00/01438

Entry of these amendments is respectfully requested.

Respectfully submitted,

By:



November 30, 2001

RHODIA INC.
259 Prospect Plains Road
CN7500,
Cranbury, NJ 08512

John Daniel WOOD
Registration No. 31,146
Tel : (609) 860-4192
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F/Brevet/RN99060 prelim.doc

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1

PROCESS FOR SYNTHESIZING POLYMERS BY CONTROLLED
FREE-RADICAL POLYMERIZATION WITH THE AID
OF HALOGENATED XANTHATES

The present invention relates to a novel
5 process for "controlled" or "living" free-radical
polymerization, giving access to block copolymers.

Block polymers are usually prepared by ionic
polymerization. A disadvantage of this type of
polymerization is that it permits the polymerization
10 only of certain types of non-polar monomers,
particularly styrene and butadiene, and that it
requires a particularly pure reaction environment, and
temperatures often lower than ambient, in order to
minimize side reactions, and the result is severe
15 operational constraints.

An advantage of free-radical polymerization
is that it is easy to implement without adhering to
excessive purity requirements, and at temperatures of
ambient or above. However, until recently there was no
20 free-radical polymerization process which could give
block polymers.

A novel process for free-radical
polymerization has now been developed: this is what is
known as "controlled" or "living" free-radical
25 polymerization. Controlled free-radical polymerization
proceeds by growth through propagation of
macroradicals. These macroradicals have a very short

lifetime and recombine irreversibly via coupling or dismutation. When the polymerization proceeds in the presence of a number of comonomers, the variation in the composition of the mixture is infinitely slow
5 compared with the lifetime of the macroradical, and therefore the chains have a random sequence of monomer units, rather than a block-type sequence.

In recently developed techniques for controlled free-radical polymerization, the extremities 10 of polymer chains can be reactivated as a radical by homolytic cleavage of a bond (for example C-O or C-halogen).

Controlled free-radical polymerization therefore has the following distinctive aspects:

15 1. the number of chains is fixed for the entire duration of the reaction,

2. all the chains grow at the same rate, resulting in:

20 • linear increase in molecular mass with conversion,

• a narrow distribution of masses,

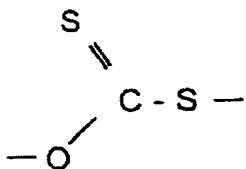
3. the average molecular mass is controlled by the molar ratio monomer/chain precursor,

25 4. the possibility of preparing block copolymers.

The controlled character is all the more pronounced if the rate of reactivation of the free-

radical chains is very great compared with the rate of growth of the chains (propagation). There are cases where this does not always apply (i.e. the reactivation rate of the free-radical chains is greater than or 5 equal to the rate of propagation) and conditions 1 and 2 are not complied with, but it is nevertheless still possible to prepare block copolymers.

The publication WO 98/58974 describes a living free-radical polymerization process giving 10 access to block copolymers by a process without UV irradiation, by using xanthate compounds, i.e. compounds having the function:



This free-radical polymerization allows 15 preparation of block polymers with the aid of any kind of monomer, without any UV source. The polymers obtained do not contain any metallic impurities detrimental to their use. They have chain-end functionalization and a low polydispersity index, lower 20 than 2, or even lower than 1.5.

It is an object of the present invention to propose a novel procedure for polymerization with the aid of new precursors of xanthate type.

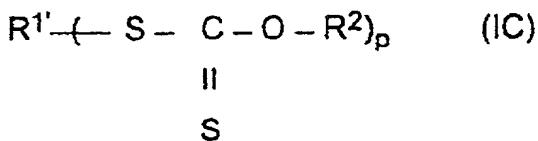
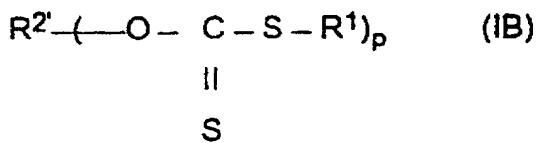
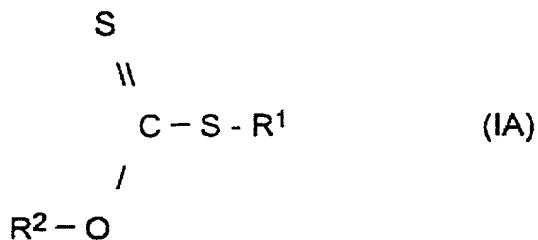
Another object is to propose a polymerization 25 process which uses precursors of xanthate type and

during the course of which the number-average molar masses M_n of the resultant polymers are well controlled, i.e. close to the theoretical values $M_{n\text{ th}}$, especially at the start of the polymerization reaction.

5 Another object is to propose a polymerization process which uses precursors of xanthate type to synthesize polymers and block copolymers whose index of polydispersity (M_w/M_n) is low, i.e. close to 1.

With this object in mind, the invention
10 provides a process for preparing polymers, characterized by bringing into contact:

- at least one ethylenically unsaturated monomer,
- at least one source of free radicals, and
- at least one compound (I) of general formula
15 (IA), (IB), or (IC):



in which:

- \mathbf{R}^2 and \mathbf{R}'^2 , represent:

- an alkyl, acyl, aryl, alkene, or alkyne group (i), or
- a carbocyclic system (ii), saturated or unsaturated, optionally aromatic, or
- a heterocyclic system (iii), saturated or unsaturated,

these groups and cyclic systems (i), (ii), and (iii) being substituted by at least one fluorine atom, chlorine atom, and/or bromine atom,

- \mathbf{R}^1 and \mathbf{R}'^1 , represent:

- an alkyl, acyl, aryl, alkene, or alkyne group (i), optionally substituted,
- or
- a carbocyclic system (ii), saturated or unsaturated, optionally substituted or aromatic,
- or
- a heterocyclic system (iii), saturated or unsaturated, optionally substituted,

where these groups and cyclic systems (i), (ii) and (iii) may be substituted by substituted phenyl groups, substituted aromatic groups, or:

alkoxycarbonyl or aryloxycarbonyl ($-\text{COOR}$), carboxy ($-\text{COOH}$), acyloxy ($-\text{O}_2\text{CR}$), carbamoyl ($-\text{CONR}_2$), cyano ($-\text{CN}$), alkylcarbonyl, alkylarylcarbonyl, arylcarbonyl,

arylalkylcarbonyl, phthalimido, maleimido, succinimido, amidino, guanidimo, hydroxyl (-OH), amino (-NR₂), halogen, allyl, epoxy, alkoxy (-OR), S-alkyl, or S-aryl groups, groups having hydrophilic or ionic character, for example the alkali metal salts of carboxylic acids, the alkali metal salts of a sulfonic acid, polyalkylene oxide chains (PEO, PPO), or cationic substituents (quaternary ammonium salts),

R representing an alkyl or aryl group, or

- a polymer chain,
- p is between 2 and 10.

The process according to the invention 15 therefore consists in bringing into contact a source of free radicals, an ethylenically unsaturated monomer, and a compound (I) of formula (IA), (IB), or (IC).

This compound (I) bears a xanthate functionality. According to the essential 20 characteristic of the invention, the xanthate functionality bears a group R² or R^{2'} which has to be substituted by at least one fluorine atom, chlorine atom, and/or bromine atom. R² and R^{2'} are preferably substituted by at least one fluorine atom, and still 25 more preferably only by fluorine atoms.

According to one preferred version, R² represents a group of formula: -CH₂R'⁵, in which R'⁵

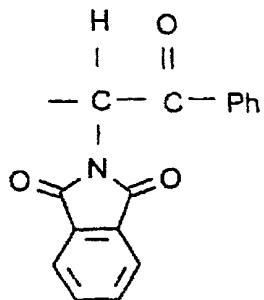
represents an alkyl group substituted by at least one fluorine atom, chlorine atom, and/or bromine atom.

According to this embodiment, preferred groups R^2 are the following:

- 5 - CH_2CF_3 ,
- $CH_2CF_2CF_2CF_3$
- $CH_2CH_2C_6F_{13}$,

According to another preferred version, R^2 represents the group $CH(CF_3)_2$.

- 10 R^1 in the formulae (IA) and (IB) preferably represents:
 - a group of formula $CR'^1R'^2R'^3$, in which:
 - R'^1 , R'^2 and R'^3 represent the groups (i), (ii), or (iii) as defined above, or
 - $R'^1 = R'^2 = H$ and R'^3 is an aryl, alkene, or alkyne group,
 - or a group of formula $-COR'^4$ in which R'^4 represents a group (i), (ii), or (iii) as defined above.
- 15 The most interesting results have been obtained for the compound (I) when R^1 is a group selected among:
 - $CH(CH_3)(CO_2Et)$
 - $CH(CH_3)(C_6H_5)$
- 20 - $CH(CO_2Et)_2$
- 25 - $C(CH_3)(CO_2Et)(S-C_6H_5)$
- $C(CH_3)_2(C_6H_5)$



in which Et represents an ethyl group and Ph represents a phenyl group.

The groups R¹ and R^{1'} may also represent a 5 polymer chain from a free-radical or ionic polymerization, or from a polycondensation. Preferred compounds of formula (IC) are those for which R^{1'} is the group - CH₂ - phenyl - CH₂ - or the group - CHCH₃CO₂CH₂CH₂CO₂CHCH₃ -.

In the preferred embodiment of the invention, the polymerization process uses a compound (I) of formula (IA). Preferred compounds of formula (IA) are ethyl α-(O-heptafluorobutylxanthyl)propionate (R¹ = CHCH₃(CO₂Et), R² = CH₂CF₂CF₂CF₃), 10 ethyl α-(O-trifluoroethylxanthyl)propionate (R¹ = CHCH₃(CO₂Et), R² = CH₂CF₃), and ethyl 15 ethyl α-(O-tridecafluoroctanylxanthyl)propionate (R¹ = CHCH₃(CO₂Et), R² = CH₂CH₂C₆F₁₃).

The compounds of formulae (IA), (IB), and 20 (IC) are easily accessible. They may particularly be obtained by reacting an alcohol R²OH with carbon disulfide CS₂ (in the presence of hydrogen hydride, for example), giving the xanthate R²O(C=S)S⁻Na⁺. This

xanthate is then reacted with an alkyl halide R^1X (X = halogen), giving the halogenated xanthate:
 $R^2O(C=S)-SR^1$.

According to the process of the invention,
5 the **free-radical source** is generally a free-radical polymerization initiator. However, for certain monomers, such as styrene, thermal initiation is sufficient to generate free radicals.

In the first case, the free-radical
10 polymerization initiator may be selected be selected among conventional initiators used in free-radical polymerization, for example one of the following initiators:

- hydrogen peroxides, such as: tert-butyl
15 hydroperoxide, cumene hydroperoxide, tert-butylperoxy acetate, tert-butylperoxy benzoate, tert-butylperoxy octoate, tert-butylperoxy neodecanoate, tert-butylperoxy isobutarate, lauroyl peroxide, tert-amylperoxy pivalate, tert-butylperoxy pivalate, dicumyl
20 peroxide, benzoyl peroxide, potassium persulfate, ammonium persulfate,

- azo compounds, such as:

2-2'-azobis(isobutyronitrile),
2,2'-azobis(2-butanenitrile), 4,4'-azobis(4-pentanoic acid), 1,1'-azobis(cyclohexanecarbonitrile), 2-(tert-butylazo)-2-cyanopropane, 2,2'-azobis[2-methyl-N-(1,1)-bis(hydroxymethyl)-2-hydroxyethyl]propionamide,

2,2'-azobis(2-methyl-N-hydroxyethyl]propionamide,
2,2'-azobis(N,N'-dimethyleneisobutyramidine)
dichloride, 2,2'-azobis(2-amidinopropane) dichloride,
2,2'-azobis(N,N'-dimethyleneisobutyramide),
5 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)-2-
hydroxyethyl]propionamide), 2,2'-azobis(2-methyl-N-
[1,1-bis(hydroxymethyl)ethyl]propionamide),
2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide],
2,2'-azobis(isobutyramide) dihydrate,
10 - redox systems including combinations such
as:

- mixtures of hydrogen peroxide, alkyl peroxide, peresters, percarbonates, and the like, and any one of the salts of iron, titanous salts, zinc

15 formaldehyde-sulfoxylate, or sodium formaldehyde-sulfoxylate, and reducing sugars,

- persulfates, perborate, or perchlorate of alkali metals or of ammonium, combined with a bisulfite of an alkali metal, such as sodium metabisulfite, and

20 reducing sugars,

- persulfate of an alkali metal combined with an arylphosphinic acid, such as benzenephosphonic acid and like compounds, and reducing sugars.

The amount of initiator to be used is
25 generally calculated so that the amount of radicals generated, as a ratio to the amount of compound (II), is at most 20 mol%, preferably at most 5%.

According to the process of the invention, the **ethylenically unsaturated monomers** are more specifically selected among styrene or its derivatives, butadiene, chloroprene, (meth)acrylic esters, vinyl 5 esters and vinyl nitriles.

(Meth)acrylic esters denote the esters of acrylic acid and of methacrylic acid with hydrogenated or fluorinated C₁-C₁₂ alcohols, preferably C₁-C₈ alcohols. Among compounds of this type mention may be 10 made of: methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, tert-butyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, isobutyl methacrylate.

15 Vinyl nitriles include more particularly those having from 3 to 12 carbon atoms, such as, in particular, acrylonitrile and methacrylonitrile.

It should be noted that styrene may be partially or completely replaced by derivatives, such 20 as alpha-methylstyrene or vinyltoluene.

Particular other ethylenically unsaturated monomers which may be used, alone or as a mixture, or which may be copolymerized with the above monomers, are:

25 - vinyl esters of a carboxylic acid, e.g. vinyl acetate, vinyl Versatate®, vinyl propionate, - vinyl halides,

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- ethylenic unsaturated mono- and dicarboxylic acids, e.g. acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, and the monoalkyl esters of dicarboxylic acids of the type
- 5 mentioned with alkanols preferably having from 1 to 4 carbon atoms, and their N-substituted derivatives,
 - amides of unsaturated carboxylic acids, e.g. acrylamide, methacrylamide, N-methylolacrylamide, or methacrylamide, N-alkylacrylamides.
- 10 - ethylenic monomers containing a sulfonic acid group and their alkali metal or ammonium salts, for example vinylsulfonic acid, vinylbenzenesulfonic acid, alpha-acrylamidomethylpropanesulfonic acid, 2-sulfoethylene methacrylate,
- 15 - amides of vinylamine, particularly vinylformamide or vinylacetamide,
 - unsaturated ethylenic monomers containing a secondary, tertiary, or quaternary amino group, or a heterocyclic group containing nitrogen, for example
- 20 vinylpyridines, vinylimidazole, aminoalkyl (meth)acrylates, and aminoalkyl(meth)acrylamides, e.g. dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, di-tert-butylaminoethyl acrylate, di-tert-butylaminoethyl methacrylate,
- 25 dimethylaminomethylacrylamide, or -methacrylamide. It is equally possible to use zwitterionic monomers, for example sulfopropyl(dimethyl)aminopropyl acrylate.

To prepare polyvinylamines, the ethylenically unsaturated monomers used are preferably amides of vinylamine, for example vinylformamide or vinylacetamide. The polymer obtained is then 5 hydrolyzed, the pH being acidic or basic.

To prepare polyvinyl alcohols, the ethylenically unsaturated monomers used are preferably vinyl esters of carboxylic acid, for example vinyl acetate. The polymer obtained is then hydrolyzed, the 10 pH being acidic or basic.

The types and amounts of polymerizable monomers used according to the present invention vary as a function of the particular final application for which the polymer is destined. These variations are 15 well known and can readily be calculated by the skilled worker.

The polymerization may be carried out in bulk, in solution, or in emulsion. It is preferably implemented in emulsion.

20 The process is preferably implemented semi-continuously.

The temperature may vary between ambient temperature and 150°C, according to the nature of the monomers used.

25 The instantaneous polymer content as a ratio of the instantaneous amount of monomer and of polymer during the polymerization is generally between 50 and

99% by weight, preferably between 75 and 99%, still more preferably between 90 and 99%. This content is maintained in a known manner, via control of the temperature, of the addition rate of the reactants, 5 and, optionally, of the polymerization initiator.

The process is generally implemented in the absence of any UV source.

The process of the invention has the advantage of allowing control of the number-average 10 molecular masses M_n of the polymers. Thus these masses M_n are close to the theoretical values $M_{n\ th}$, where $M_{n\ th}$ is given by the following formula

$$M_{n\ th} = \frac{[M]_0}{[P]_0} \frac{X}{100} M_0$$

15 in which:

$[M]_0$ represents the initial molar concentration of monomer

$[P]_0$ represents the initial concentration of precursor compound

20 X represents the monomer conversion expressed as a percentage

M_0 represents the molar mass of the monomer (g/mol).

According to the present invention, the 25 control of M_n is particularly apparent at the start of the polymerization.

In addition, the polymerization process according to the present invention leads to polymers with a low polydispersity index ($I_p = M_w/M_n$, where M_w : weight-average molecular mass), close to 1.

5 The invention therefore also provides **polymers** obtainable by the process consisting of bringing at least one ethylenically unsaturated monomer into contact with at least one source of free radicals and at least one compound of formula (IA), (IB), or
10 (IC).

The polymers generally have a polydispersity index of at most 2, preferably of at most 1.5.

15 The invention also provides a **process for preparing multiblock polymers**, in which the implementation of the polymerization process described above is repeated at least once, using:

16 - compared with the preceding implementation, different monomers, and
- instead of the compound (I) of formula
20 (IA), (IB), or (IC), the polymer from the preceding implementation, known as a precursor polymer.

The complete process for synthesizing a block polymer according to the invention may therefore consist in:

25 (1) synthesizing a precursor polymer by bringing into contact an ethylenically unsaturated

monomer, a source of free radicals, and a compound of formula (IA), (IB), or (IC),

(2) using the precursor polymer obtained in step (1) to prepare a diblock polymer by bringing this 5 precursor polymer into contact with a new ethylenically unsaturated monomer and a source of free radicals.

This step (2) may be repeated as many times as desired with new monomers, to synthesize new blocks and obtain a multiblock polymer.

10 If the implementation is repeated once, a triblock polymer will be obtained, and if it is repeated a second time, a "quadriblock" polymer will be obtained, and so on. With each fresh implementation, therefore, the product obtained is a block polymer 15 having an additional polymer block.

To prepare multiblock polymers, therefore, the process consists in repeating the implementation of the preceding process a number of times on the block polymer coming from each preceding implementation, with 20 different monomers.

The compounds of formula (IB) and (IC) are particularly interesting because they allow a polymer chain to be grown at at least two active sites. With compounds such as these it is possible to economize on 25 polymerization steps to obtain a copolymer of n blocks. Thus, if the value of p is 2 in the formula (IB) or (IC), the first block is obtained by polymerizing a

monomer M1 in the presence of the compound of formula (IB) or (IC). This first block may then grow at each of its extremities via polymerization of a second monomer M2. A triblock copolymer is obtained, and this triblock 5 polymer itself can grow at each of its extremities via polymerization of a third monomer M3. Thus, a "pentablock" copolymer is obtained in only three steps. If p is greater than 2, the process can give homopolymers or block copolymers whose structure is 10 10 "multi-branched" or hyperbranched.

According to this process for preparing multiblock polymers, if it is desired that the block polymers obtained are homogeneous and do not have a composition gradient, and if all of the successive 15 polymerizations are carried out in the same reactor, it is essential that all the monomers used in one step are consumed before the polymerization of the next step starts, e.g. before the new monomers are introduced.

As for the process for polymerizing a 20 monoblock polymer, this process for polymerizing block polymers has the advantage of leading to block polymers having a low polydispersity index. It also allows control of the molecular mass of block polymers.

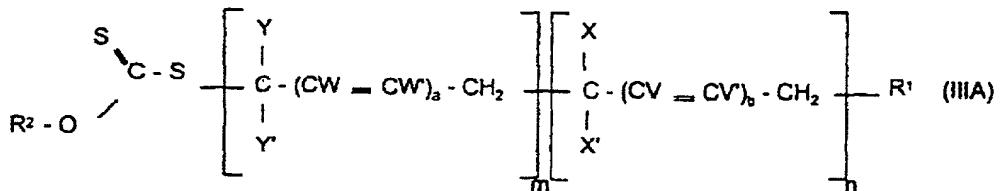
The invention therefore provides block 25 polymers obtainable by the preceding process.

These block polymers generally have a polydispersity index of at most 2, preferably of at most 1.5.

The invention particularly provides block 5 polymers which have at least two polymer blocks selected among the following partners:

- polystyrene/polymethyl acrylate
- polystyrene/polyethyl acrylate,
- polystyrene/polytert-butyl acrylate,
- 10 - polyethyl acrylate/polyvinyl acetate,
- polybutyl acrylate/polyvinyl acetate
- polytert-butyl acrylate/polyvinyl acetate.

When use is made of compounds of formula (IA), the block polymers obtained have a structure of 15 the type:



in which:

- R², R¹ are as defined above,
- V, V', W and W' are identical or different 20 and represent: H, an alkyl group, or a halogen,
- X, X', Y, and Y' are identical or different and represent H, a halogen, or an R³, OR³, O₂COR³, NHCOH, OH, NH₂, NHR³, N(R³)₂, (R³)₂N⁺O⁻,

NHCOR³, CO₂H, CO₂R³, CN, CONH₂, CONHR³ or CONR³₂

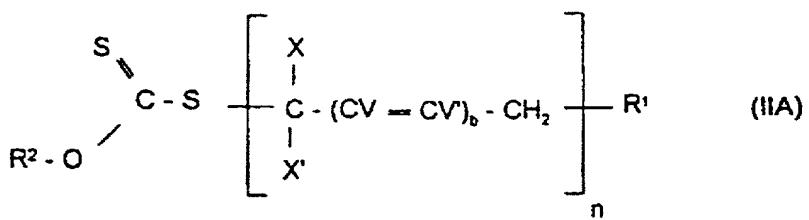
group, in which R³ is selected among alkyl, aryl, aralkyl, alkaryl, alkene, or organosilyl groups, optionally

5 perfluorinated, and optionally substituted by one or more carboxy, epoxy, hydroxyl, alkoxy, amino, halogen, or sulfonic groups,
 - a and b are identical or different and have values 0 or 1,

10 - m and n are identical or different and are greater than or equal to 1, and if one of these is greater than 1, the repeat units are identical or different.

These block polymers are the result of
 15 bringing into contact:

- an ethylenically unsaturated monomer of
 formula: CYY' (= CW - CW')_b = CH₂,
 - a precursor polymer of general formula
 (IIA) :



- a source of free radicals.

The polymer (IIA) is the result of bringing into contact an ethylenically unsaturated monomer of formula: CXX' (= CV - CV')_a = CH₂, a compound (I) of
 25 general formula (IA) and a source of free radicals.

In the formula (IIA), n is preferably greater than or equal to 6.

Particularly preferred compounds (IIA) are homopolymers of styrene ($Y' = H$, $Y = C_6H_5$, $b = 0$), of 5 methyl acrylate ($Y' = H$, $Y = COOMe$, $b = 0$), of ethyl acrylate ($Y' = H$, $Y = COOEt$, $b = 0$), of butyl acrylate ($Y' = H$, $Y = COOBu$, $b = 0$), of tert-butyl acrylate ($Y' = H$, $Y = COtBu$, $b = 0$), of vinyl acetate ($Y' = H$, $Y = OCOMe$, $b = 0$), of acrylic acid ($Y' = H$, $Y = COOH$, 10 $b = 0$), and for which:

- $R^1 = CHCH_3(CO_2Et)$, $CH(CO_2Et)_2$, or $C(CH_3)_2(C_6H_5)$, and

- $R^2 = -CH_2CF_3$, $-CH_2CF_2CF_2CF_3$, or $CH_2CH_2C_6F_{13}$.

The examples below illustrate the invention 15 but do not restrict its scope.

Figure 1 gives curves for M_n and M_w/M_n as a function of the conversion rate of the ethyl acrylate monomer when using a xanthate according to the invention and of a xanthate according to the prior art.

20 Figure 2 gives curves for M_n and M_w/M_n as a function of the conversion rate of the styrene monomer when using a xanthate according to the invention and of a xanthate according to the prior art.

EXAMPLES**EXAMPLES 1 - SYNTHESES OF PRECURSORS OF FORMULA (IA)****(xanthates)****Example 1.1 - Synthesis of the precursor ethyl α -(O-****heptafluorobutylxanthyl)propionate (A)**

1 g (5 mmol) of heptafluorobutanol is dissolved in 10 ml of DMF (N,N-dimethylformamide) in a glass flask. 0.6 ml (10 mmol) of CS_2 is added. The solution is cooled to 0°C, and then 0.24 g (5 mmol) of 10 NaH is added. After 1 hour of stirring at 0°C, 0.6 ml (4.5 mmol) of ethyl 2-bromopropionate is added. The solution is stirred for 1 hour at 0°C, then 2 hours at ambient temperature, before being diluted with ethyl ether. It is then washed with water, and then with 15 brine. The organic phase is concentrated in vacuo, and then the crude product is purified through a column (9/1: heptane/ethyl acetate). 1.5 g (88% yield) of product A are isolated.

20 Example 1.2 - Synthesis of the precursor ethyl α -(O-trifluoroethylxanthyl)propionate (B)

2 g (20 mmol) of trifluoroethanol are dissolved in 40 ml of DMF in a glass flask. 2.4 ml (40 mmol) of CS_2 are added. The solution is cooled to 25 0°C, and then 0.96 g (20 mmol) of NaH is added. After 1 hour of stirring at 0°C, 2.34 ml (18 mmol) of ethyl 2-bromopropionate is added. The solution is stirred for

1 hour at 0°C, then two hours at ambient temperature, before being diluted with ethyl ether. It is then washed with water, and then with brine. The organic phase is concentrated in vacuo, and then the crude 5 product is purified through a column (9/1: heptane/ethyl acetate). 3.4 g (69% yield) of xanthate B are isolated.

Example 1.3 - Synthesis of the precursor ethyl a-(O-tridecafluorooctanyl)propionate (C)

10 1.1 ml (5 mmol) of tridecafluorooctanol are dissolved in 10 ml of DMF in a glass flask. 0.6 ml (10 mmol) of CS₂ is added. The solution is cooled to 0°C, and then 0.24 g (5 mmol) of NaH is added. After 1 hour of stirring at 0°C, 0.6 ml (4.5 mmol) of ethyl 15 2-bromopropionate is added. The solution is stirred for 1 hour at 0°C, then 2 hours at ambient temperature, before being diluted with ethyl ether. It is then washed with water, and then with brine. The organic phase is concentrated in vacuo, and then the crude 20 product is purified through a column (9/1: heptane/ethyl acetate). 2.27 g (93% yield) of xanthate C are isolated.

EXAMPLES 2 - SYNTHESES OF POLYMERS (homopolymers)

25 These examples show that the free-radical polymerization is controlled due to the use of the xanthates of the invention.

In the examples below the polymers are analyzed by GPC with THF as eluting solvent; M_n is expressed in polystyrene equivalents (g/mol).

Example 2.1 - Homopolymerization of ethyl acrylate in

the presence of B.

- 0.02 mmol of azobisisobutyronitrile (AIBN) (3.38 mg),
- 54.9 mmol of ethyl acrylate (5.5 g)
- 0.69 mmol of xanthate B (0.19 g)
- 10 - 5.97 cm³ of toluene (5.17 g).

are introduced into a glass flask.

The solution obtained is divided into eight fractions distributed over the same number of Carius tubes. The tubes are connected to a vacuum line, and 15 immersed in liquid nitrogen, and then the contents of each tube are subjected to three cycles of "freezing/vacuum/back to ambient" to degas the tubes. They are then vacuum-sealed. After return to ambient, they are immersed in an oil bath preheated to 80°C. 20 They are taken from the oil bath in sequence at regular intervals of time (t) and immersed in liquid nitrogen so that the polymerization is ended and the tubes can be analyzed.

The polymer is recovered by opening the tube 25 and then evaporating traces of residual monomer.

Both of the following are tested:

- precursor conversion by GPC (UV detection),
- and
- monomer conversion by gravimetric analysis.

The results obtained are reported in table 1
5 and figure 1.

Table 1

Test	t (min)	Monomer conversion (%)	Precursor conversion (%)	M_n	M_w/M_n
1	5	<1			
2	15	4.2	36.3	2 790	1.98
3	20	11	72.6	2 940	2.00
4	25	25.7	73.4	3 600	1.81
5	35	46.4	92	5 115	1.58
6	53	84.1	>99	6 756	1.52
7	80	89.9	>99	7 716	1.43
8	140	91.8	>99	7 946	1.42

Figure 1 compares the results obtained with
the xanthate B and those obtained with ethyl
10 a-(O-ethylxanthyl)propionate (R^2 = ethyl), under the
same conditions of initial molar concentrations and
temperature.

The value of M_n is found to be better
controlled with xanthate B: the value approaches the
15 theoretical value ($M_{n\ th}$) from the start of the
polymerization, unlike in the case of the

polymerization with the xanthate of the prior art (ethyl α -(O-ethylxanthyl)propionate).

In addition, the value of M_w/M_n tends rapidly toward 1 in the case of xanthate B, whereas this value 5 remains stable at more than 1.6 for the xanthate of the prior art (ethyl α -(O-ethylxanthyl)propionate).

Example 2.2 - Homopolymerization of ethyl acrylate in the presence of C.

1.08 ml are taken from a solution composed of 10 3.9 mg of AIBN and 7.5 ml of ethyl acrylate. This fraction is added to 68.1 mg (0.126 mmol) of xanthate C in a Carius tube. The tube is degassed, then vacuum-sealed. The reaction takes 21 h at 80°C.

The monomer conversion is 95%.

15 The xanthate conversion is 100%.

The value of M_n is 9 400 g/mol

The value of M_w/M_n is 1.48.

At a high conversion rate, the value of the polymerization index is found to be low, and close to 20 1.

Example 2.3 - Homopolymerization of ethyl acrylate in the presence of A.

- 0.01 mmol of AIBN (1.69 mg),
- 31.9 mmol of ethyl acrylate (3.192 g)
- 25 - 0.4 mmol of xanthate A (0.15 g)
- 3.47 cm³ of toluene (3 g).

are introduced into a glass flask.

Five tubes are prepared and vacuum-sealed in a manner similar to that used in example 2.1. The analyses are carried out in the same manner.

The results are reported in table 2.

5

Table 2

Test	t (min)	Monomer conversion (%)	Precursor conversion (%)	M_n	M_w/M_n
1	15	<1			
2	25	11.3	42.6	3 603	1.76
3	35	24.7	70.4	4 590	1.62
4	45	45.3	93.9	5 934	1.55
5	90	81.8	>99	8 380	1.41

At high conversion, the values of the polydispersity index is found to be close to 1.4.

Example 2.4. - Homopolymerization of styrene in the

10 **presence of B.**

- 3.016 g (3.32 ml, 28.9 mmol) of styrene
- 0.1 g (0.36 mmol) of xanthate B
- 3.32 ml of toluene.

are introduced into a glass flask.

15

The mixture obtained is separated into 5 fractions distributed among the same number of Carius tubes. These are degassed, then vacuum-sealed, and then placed in an oven kept at 110°C. At regular intervals

of time the tubes are removed, cooled, and then opened. The results obtained are given in table 3 and figure 2.

Table 3

Test	T (hours)	Monomer conversion (%)	M_n	M_w/M_n
1	2	7.8	2 660	1.93
2	5.33	16	2 940	1.89
3	16.25	28	3 520	1.77
4	25.5	41.1	3 830	1.76
5	89.5	65.8	5 600	1.57

5 Figure 2 compares the results obtained with xanthate B and those obtained with ethyl α -(O-ethylxanthyl)propionate (R^2 = ethyl), under the same conditions of initial molar concentrations and temperature.

10 The value of M_n is found to be better controlled with xanthate B: the value approaches the theoretical value ($M_{n\ th}$) from the start of the polymerization, unlike in the case of the polymerization with the xanthate of the prior art 15 (ethyl α -(O-ethylxanthyl)propionate).

In addition, the value of M_w/M_n tends rapidly toward 1 in the case of xanthate B, whereas this value remains stable at about 2 for the xanthate of the prior art (ethyl α -(O-ethylxanthyl)propionate).

Example 2.5 - Homopolymerization of vinyl acetate in the presence of B.

5

- 4.73 g (55 mmol) of vinyl acetate
- 0.19 g (0.69 mmol) of xanthate B
- 3.38 mg (0.02 mmol) of AIBN.

are introduced into a glass tube.

The tube is degassed, then vacuum-sealed.

After 8 h 20 at 60°C, the tube is opened and the polymer is analyzed:

10

- monomer conversion: 11.3%
- $M_n = 740$ g/mol
- $M_w/M_n = 1.19$.

Under the same conditions of temperature and of initial concentration, it is found that the xanthate 15 of the prior art (ethyl α -(O-ethylxanthyl)propionate) allows M_n to be controlled (< 1 000 g/mol) to approximately 10% monomer conversion, while the value of M_w/M_n remains in the vicinity of 1.5.

20 **Example 2.6 - Homopolymerization of styrene in the presence of B.**

25 are introduced into a glass tube.

- 0.81 g (0.9 ml, 7.8 mmol) of styrene
- 27.7 mg (0.1 mmol) of xanthate B
- 0.93 ml of toluene.

The tube is degassed, then vacuum-sealed.

After 114 hours at 120°C, the tube is opened and the polymer is characterized. The results are as follows:

- monomer conversion: 84.4%
- 5 - $M_n = 7\ 500$ g/mol
- $M_w/M_n = 1.57$

At high conversion the value of the polymerization index is found to be low and close to 1.

10 **Example 2.7 - Homopolymerization of ethyl acrylate in the presence of B.**

- 1.61 g (1.75 ml, 16.1 mmol) of ethyl acrylate
- 52.6 mg (0.19 mmol) of xanthate B
- 15 - 1.84 ml of toluene.

are introduced into a glass tube.

The tube is degassed, then vacuum-sealed.

After 20 hours at 80°C, the tube is opened and the polymer is characterized. The results are as follows:

- 20 - monomer conversion: 88.1%
- $M_n = 8\ 200$ g/mol
- $M_w/M_n = 1.69$

At high conversion the value of the polymerization index is found to be low and close to 1.

EXAMPLES 3 - SYNTHESES OF BLOCK POLYMERS**Example 3.1 - Synthesis of a polystyrene-b-ethyl polyacrylate diblock copolymer**

5 - 0.25 g of the polystyrene described in example 2.6

- 0.3 g (3 mmol) of ethyl acrylate
- 0.15 mg (9.10^{-7} mol) of AIBN
- 0.57 ml of toluene

are introduced into a glass tube.

10 The tube is degassed, then vacuum-sealed.

After 20 h at 120°C, the tube is opened and the copolymer is characterized. The results are as follows:

15

- monomer conversion: 40.1%
- $M_n = 12\ 400$ g/mol
- $M_w/M_n = 1.45$.

Under the same conditions of temperature and of initial concentration, it is found that the xanthate of the prior art (ethyl α -(O-ethylxanthyl)propionate) leads to a diblock copolymer having a polydispersity 20 index of 1.8.

Example 3.2 - Synthesis of a polystyrene-b-butyl polyacrylate diblock copolymer

25 - 0.175 g of the polystyrene described in example 2.6

- 0.27 g (2.12 mmol) of butyl acrylate
- 0.15 mg (9.10^{-7} mol) of AIBN

- 0.57 ml of toluene

are introduced into a glass tube.

The tube is degassed, then vacuum-sealed.

After 20 h at 120°C, the tube is opened and the

5 copolymer is characterized. The results are as follows:

- monomer conversion: 42.4%
- $M_n = 12\ 100$ g/mol
- $M_w/M_n = 1.66$.

10 **Example 3.3 - Synthesis of a polyethyl acrylate-b-polyvinyl acetate diblock copolymer**

- 0.2 g of the polyethyl acrylate described
in example 2.7

- 0.2 g (2.3 mmol) of vinyl acetate
- 0.44 mg ($3.6 \cdot 10^{-6}$ mol) of AIBN
- 0.32 g of methyl ethyl ketone

are introduced into a glass tube.

The tube is degassed, then vacuum-sealed.

After 20 h at 80°C, the tube is opened and the polymer

20 is characterized. The results are as follows:

- monomer conversion: 71%
- $M_n = 13\ 300$ g/mol
- $M_w/M_n = 1.66$.

Example 3.4 - Synthesis of a polystyrene-b-polyvinyl acetate diblock copolymer

- 0.2 g of the polystyrene described in example 2.6
- 5 - 0.2 g (2.3 mmol) of vinyl acetate
- 0.44 mg ($3.6 \cdot 10^{-6}$ mol) of AIBN
- 0.32 ml of toluene

are introduced into a glass tube.

The tube is degassed, then vacuum-sealed.

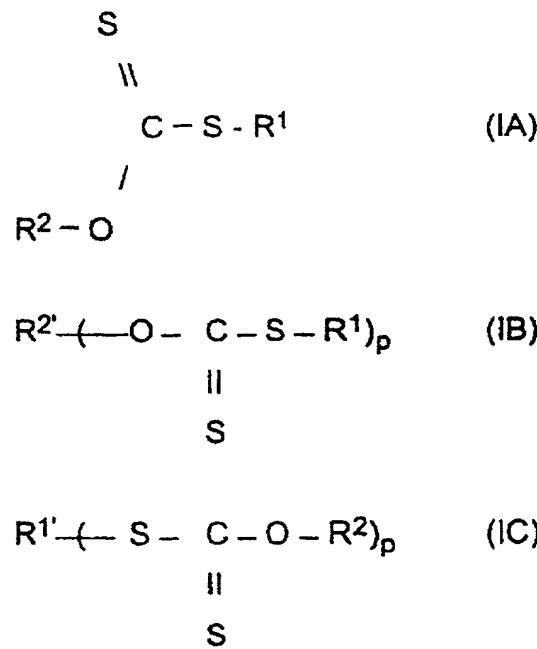
10 After 20 h at 80°C, the tube is opened and the polymer is characterized. The results are as follows:

- monomer conversion: 74%
- $M_n = 12\ 800$ g/mol
- $M_w/M_n = 1.61$.

CLAIMS

1. A process for preparing polymers, characterized by bringing into contact:

- at least one ethylenically unsaturated monomer,
- 5 - at least one source of free radicals, and
- at least one compound of general formula (IA), (IB), or (IC):



in which:

10

- R^2 and R^2' , represent:

- an alkyl, acyl, aryl, alkene, or alkyne group (i), or
- a carbocyclic system (ii), saturated or unsaturated, optionally aromatic, or
- a heterocyclic system (iii), saturated or unsaturated,

15

these groups and cyclic systems (i), (ii), and (iii) being substituted by at least one fluorine atom, chlorine atom, and/or bromine atom,

- \mathbf{R}^1 and \mathbf{R}^1' represent:

5 • an alkyl, acyl, aryl, alkene, or alkyne group (i), optionally substituted,

or

• a carbocyclic system (ii), saturated or unsaturated, optionally substituted or

10 aromatic,

or

• a heterocyclic system (iii), saturated or unsaturated, optionally substituted,

where these groups and cyclic systems (i), (ii)

15 and (iii) may be substituted by substituted phenyl groups, substituted aromatic groups, or:

alkoxycarbonyl or aryloxycarbonyl (-COOR),

carboxy (-COOH), acyloxy (-O₂CR), carbamoyl

(-CONR₂), cyano (-CN), alkylcarbonyl,

20 alkylarylcarbonyl, arylcarbonyl,

arylalkylcarbonyl, phthalimido, maleimido,

succinimido, amidino, guanidino, hydroxyl

(-OH), amino (-NR₂), halogen, allyl, epoxy,

alkoxy (-OR), S-alkyl, or S-aryl groups, groups

25 having hydrophilic or ionic character, for

example the alkali metal salts of carboxylic

acids, the alkali metal salts of a sulfonic

acid, polyalkylene oxide chains (PEO, PPO), or cationic substituents (quaternary ammonium salts),

R representing an alkyl or aryl group, or

5 • a polymer chain,

- p is between 2 and 10.

2. The process as claimed in the preceding claim, characterized in that R² and R^{2'} are substituted by at least one fluorine atom.

10 3. The process as claimed in any one of the preceding claims, characterized in that R² represents a group of formula: -CH₂R'⁵, in which R'⁵ represents an alkyl group substituted by at least one fluorine atom, chlorine atom, and/or bromine atom.

15 4. The process as claimed in the preceding claim, characterized in that R² is selected among the following groups:

- CH₂CF₃,
- CH₂CF₂CF₂CF₃
- 20 - CH₂CH₂C₆F₁₃.

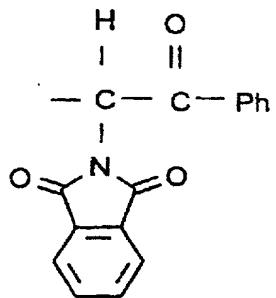
5. The process as claimed in any one of the preceding claims, characterized in that R¹ represents:

- a group of formula CR'¹R'²R'³, in which:
 - R'¹, R'² and R'³ represent the groups (i), (ii), or 25 (iii) as defined above, or
 - R'¹ = R'² = H and R'³ is an aryl, alkene, or alkyne group,

- or a -COR'⁴ group in which R'⁴ represents a group (i), (ii), or (iii).

6. The process according to the preceding claim, characterized in that R¹ is selected among the 5 groups:

- CH(CH₃) (CO₂Et)
- CH(CH₃) (C₆H₅)
- CH(CO₂Et)₂
- C(CH₃) (CO₂Et) (S-C₆H₅)
- 10 - C(CH₃)₂ (C₆H₅)



7. The process as claimed in any one of the preceding claims, characterized in that the 15 polymerization uses a compound of formula (IA).

8. The process as claimed in the preceding claim, characterized in that the compound of formula (IA) is selected among ethyl α-(O-heptafluorobutylxanthyl)propionate 20 (R¹ = CHCH₃(CO₂Et), R² = CH₂CF₂CF₂CF₃), ethyl α-(O-trifluoroethylxanthyl)propionate (R¹ = CHCH₃(CO₂Et), R² = CH₂CF₃), and

ethyl α -(0-tridecafluoroctanyl xanthyl) propionate
($R^1 = \text{CHCH}_3(\text{CO}_2\text{Et})$, $R^2 = \text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13}$).

9. The process as claimed in any one of the preceding claims, characterized in that the 5 ethylenically unsaturated monomer is selected among: styrene or its derivatives, butadiene, chloroprene, (meth)acrylic esters, and vinyl nitriles.

10. The process as claimed in any one of the preceding claims, characterized in that the 10 ethylenically unsaturated monomer is selected among vinyl acetate, vinyl Versatate®, and vinyl propionate.

11. A polymer obtainable by the process which consists in bringing an ethylenically unsaturated monomer into contact with a source of free radicals and 15 a compound of formula (IA), (IB), or (IC).

12. The polymer as claimed in the preceding claim, characterized in that it has a polydispersity index of at most 2, preferably of at most 1.5.

13. A process for preparing multiblock 20 polymers, characterized in that the implementation of the process as claimed in one of claims 1 to 10 is repeated at least once, using:

- compared with the preceding implementation, different monomers, and
25 - instead of the precursor compound of formula (IA), (IB), or (IC), the block polymer from the preceding implementation.

14. A block polymer obtainable by the process as claimed in the preceding claim.

15. The block polymer as claimed in the preceding claim, characterized in that it has an index of polydispersity of at most 2, preferably of at most 1.5.

16. The block polymer as claimed in claim 11 or 12, characterized in that it has at least two polymer blocks selected among the following partners:

- 10 - polystyrene/polymethyl acrylate
- polystyrene/polyethyl acrylate,
- polystyrene/polytert-butyl acrylate,
- polyethyl acrylate/polyvinyl acetate,
- polybutyl acrylate/polyvinyl acetate

15 - polytert-butyl acrylate/polyvinyl acetate.

**PROCESS FOR SYNTHESIZING POLYMERS BY CONTROLLED FREE-RADICAL
POLYMERIZATION WITH THE AID OF HALOGENATED XANTHATES**

Abstract of the Disclosure

The invention concerns a method for preparing polymers, which consists in contacting: an ethylenically unsaturated monomer; a source of free radicals; and a halogenated xanthate.

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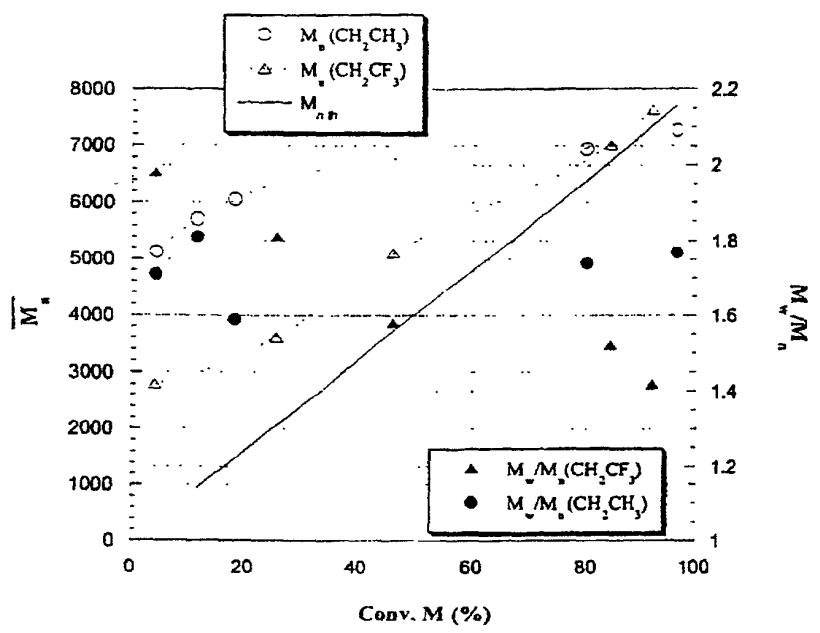


Figure 1

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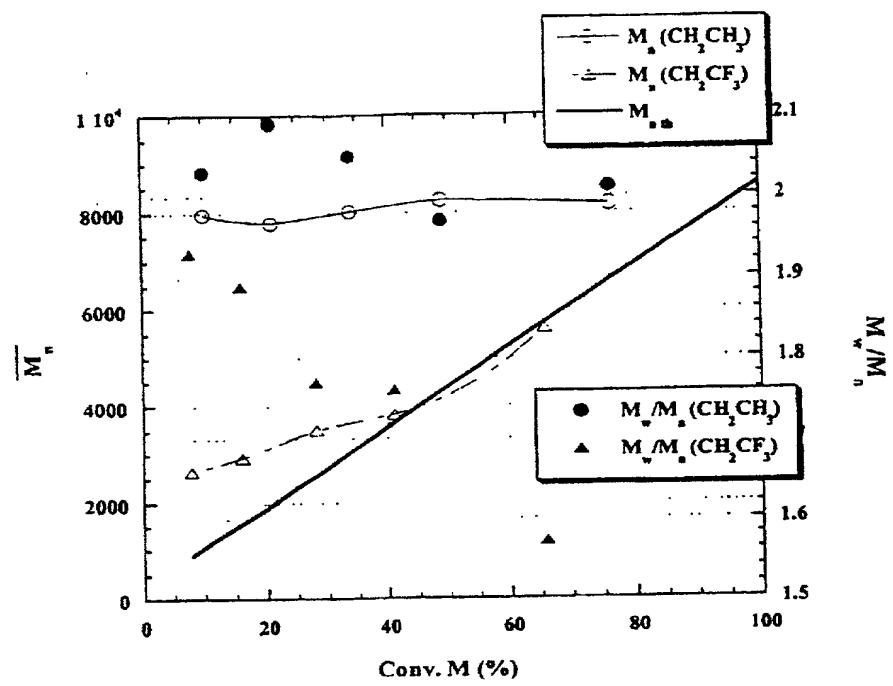


Figure 2